

Sept. 12, 1972

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3,690,883

METHOD OF FORMING A LITHO PLATE BY DIFFUSION TRANSFER

Filed Jan. 30, 1970

2 Sheets-Sheet 1

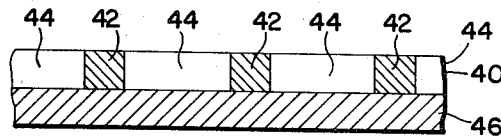
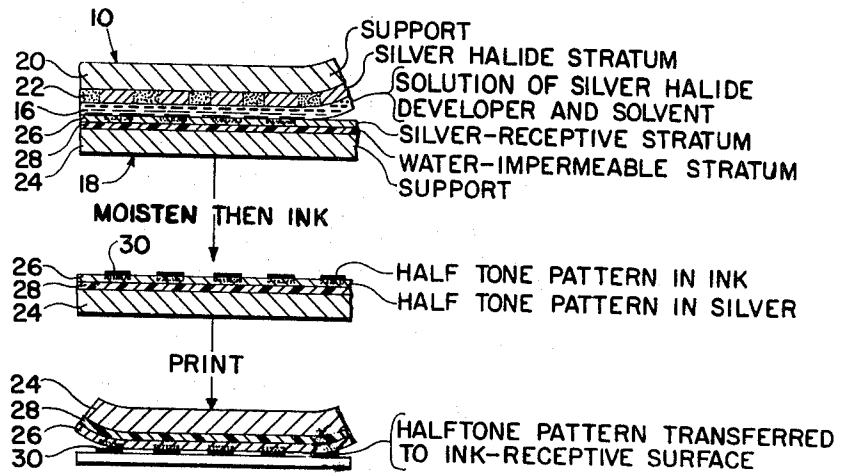


FIG. 2

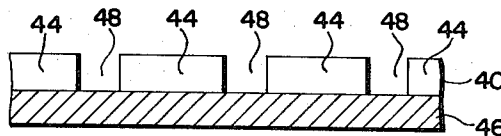


FIG. 3

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2 Sheets-Sheet 2

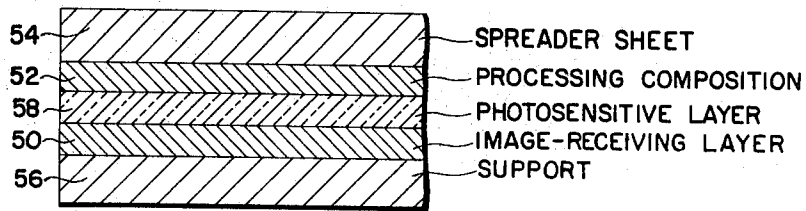


FIG. 4

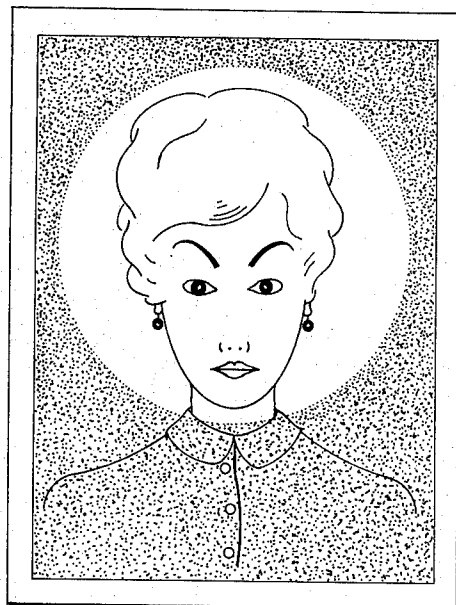


FIG. 5



FIG. 6

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3,690,883

**METHOD OF FORMING A LITHO PLATE BY
DIFFUSION TRANSFER**Albert L. Hyland, Jr., Wayland, Mass., assignor to
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Int. Cl. G03c 5/54

U.S. Cl. 96—29 L

11 Claims

ABSTRACT OF THE DISCLOSURE

A method for selectively eliminating hydrophobic portions of a photolithographic printing surface to modify the information contained in said surface or add information to said surface. Essentially, the method involves the step of applying a hydrophilic coating to selected portions of the hydrophobic printing pattern contained in said plate.

BACKGROUND OF THE INVENTION**(1) The field of the invention**

This invention relates to photolithography. More precisely, the invention disclosed herein relates to a convenient, novel method for selectively modifying the information contained in a photolithographic printing surface.

(2) Description of the prior art

Lithography is the printing of reproductions from a surface wherein ink is selectively distributed on a surface corresponding to the matter to be printed therefrom. The selective distribution of the printing ink is achieved by reason of differentials in the ink resistivity of the surface. It is known that diffusion transfer photography can be employed to produce photolithographic printing surfaces.

One particularly useful procedure for obtaining a printing master by silver diffusion transfer is described in U.S. Pat. No. 3,220,837, issued to Edwin H. Land and Meroe M. Morse. This patent is predicated upon the discovery that if the silver transfer print has areas that contain silver concentrated primarily at the surface of the silver-receptive stratum in thin but essentially continuous, dense masses and other areas that are substantially silver-free or which do not contain these dense masses of silver, the areas containing these dense silver deposits are oleophilic and hence are inkable or wettable with an oleophilic or greasy ink; whereas the other areas which are initially hydrophilic retain their hydrophilic character and hence are not so inkable. In other words, a silver transfer print of this description is characterized as being such that when an oleophilic ink is applied uniformly over the surface of the print, this ink adheres only to the areas of dense silver deposits, so that the silver transfer image may be characterized further as being selectively inkable with an oleophilic or greasy ink of the type commonly employed in lithography. Thus, following application of the oleophilic ink, the inked silver transfer image may be employed in standard lithographic procedures to provide one or more ink reproductions of the original subject matter.

The copending application of Edwin H. Land, Ser. No. 676,510, filed Oct. 19, 1967, describes and claims another system for forming a printing master by silver diffusion transfer. In the procedures described in this copending application, the image-receiving element employed to prepare the print comprises a silver-receptive stratum having a plurality of layers containing progressively increasing concentrations of silver precipitating nuclei as the distance from the surface increases, the greatest concentration of silver precipitating nuclei being in the layer closest to the hydrophobic support or under layer containing the silver-receptive stratum. In silver diffusion transfer processes employing such an image-receiving element, the

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silver is deposited deeper into the receiving layer than is obtained in processes such as those described in the aforementioned patent wherein the silver is deposited primarily at the surface of the silver-receptive stratum. In accordance with the procedures disclosed in the aforementioned copending application, development is effected in the presence of an anti-adhesion reagent and following silver image formation, the areas of dense silver deposit and corresponding areas of the silver-receptive stratum are selectively removed to provide an intaglio or etched image in terms of this image-wise removal of silver and corresponding areas of the silver-receptive stratum. This image may then be selectively inked with an oleophilic ink which selectively adheres to the hydrophobic underlayer in areas where the silver deposit and silver-receptive stratum have been removed.

Occasionally, it is necessary or desirable to eliminate or otherwise modify the information contained in the oleophilic, e.g., hydrophobic printing areas of a lithographic printing plate. For example, if the information is in the form of a portrait, one may desire to alter the hydrophobic printing areas of the plate to provide a border of a desired artistic design about the portrait by eliminating hydrophobic printing areas corresponding to the design of the border. Also, by removing hydrophobic printing areas, additional information can be installed in the plate. For example, a pattern of ordinates or printed information or written information such as an autograph can be added to a lithographic printing plate by eliminating selective hydrophobic portions of the plate in a pattern corresponding to the information to be added. The remaining hydrophobic printing portion(s), surrounding the portion(s) eliminated, will render the pattern visible.

SUMMARY OF THE INVENTION

In accordance with the present invention, a method is presented for conveniently eliminating or selectively modifying the hydrophobic portions of a lithographic printing plate. Essentially, the method of the present invention involves the step of selectively applying a hydrophilic coating to those portions of the hydrophobic printing plate which are intended to be eliminated. The coating can be most conveniently applied to the selected hydrophobic portion in the form of a dispersion or solution by such instruments as a brush, pen or stamp or the like. The coating can also be applied in a solid or semisolid form. For example, a releasable hydrophilic coating deposited on a ribbon, strip or other suitable substrate can be transferred to selected portions of the hydrophobic printing surface by pressure from a stamp or typewriter.

The particular hydrophilic coating material employed in the practice of the present invention is not in itself especially critical. For example, suitable coatings can be produced or cast from solutions or dispersions of hydrophilic materials. The hydrophilic material may be a solution or dispersion of a hydrophilic polymeric material such as polyvinyl alcohol, carboxymethyl cellulose, or the like. Also, a solution or dispersion of such materials as water-glass or colloidal or finely divided siliceous materials such as oxides of silica, particularly those in the form of silica acids like silica aerogel, and mineral silicates such as mica and talc may be employed. As examples of suitable siliceous materials, mention may be made of "Syton," trademark of Monsanto Chemical Co. for a milky-white, stable, 15% colloidal dispersion of silica in water, sp. gr. 1.10; "Santocel" (trademark of Consanto Chemical Co. for a lightweight porous silica aerogel from which the water has been removed by a process that does not destroy the original gel structure, apparent density, 6.5-9.75 lb./cu. ft.); and "Ludox" (trademark of E. I. duPont, deNemours & Co. for an

aqueous colloidal sol containing approximately 35% SiO_2 with less than 0.5% Na_2O as stabilizer, sp. gr. 1.21).

A thickening agent can be included in the dispersion or solution of the hydrophilic material. The most suitable are water-soluble polymeric thickening agents such as gelatin, polyvinyl acetate, polyvinyl alcohol or the like. An especially suitable material for producing hydrophilic coatings is an aqueous solution of ½% gelatin mixed in a 3:1 ratio with commercially available "Ludox" (30% silica, L.S. type).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention and preferred embodiments thereof will be better understood by reference to FIGS. 1-6 wherein FIG. 1 shows successive, exaggerated, sectional views of a photosensitive medium and receiving sheet undergoing a sequence of operations to provide a photolithographic printing surface in accordance with the procedure of U.S. Pat. No. 3,220,837.

FIG. 2 is an enlarged, diagrammatic fragmentary sectional view illustrating a silver transfer image.

FIG. 3 is a similar view illustrating the image of FIG. 2 after treatment in accordance with the teachings of the invention of the aforementioned U.S. patent application Ser. No. 676,510 to provide a photolithographic printing surface.

FIG. 4 is a similar view of a unitary film unit useful in the practice of the invention of U.S. patent application Ser. No. 676,510 during one stage of processing thereof.

FIG. 5 is an illustration of a photolithographic printing surface produced in accordance with the procedure illustrated in FIG. 1 and wherein a selected portion of the hydrophobic printing pattern is eliminated in accordance with the practice of the present invention.

FIG. 6 is an illustration of a printed reproduction of the photolithographic plate of FIG. 5.

Referring now to FIG. 1, a photosensitive medium 10 is shown which has been exposed to an image pattern of activating radiation. A processing composition 16 is shown spread between photosensitive medium 10 and an image-receptive sheet 18, for example, by advancing the sheets between a pair of pressure-applying rollers (not shown). Photosensitive medium 10 comprises a support 20 and a silver halide stratum 22. Image-receptive sheet 18 comprises a support 24 and a silver-receptive stratum 26. Processing composition 16 is an aqueous alkaline solution of a silver halide developer, a silver halide solvent and a viscosity-increasing film-forming material. Once spread, composition 16 forms a negative image pattern in silver halide stratum 22 by reducing exposed or developable silver halide to silver, and forms a positive image pattern by reacting with unreacted silver halide to form a complex silver salt which migrates to stratum 26 where it is reduced to silver. Accordingly, when sheet 10 together with layer of processing composition 16 is stripped from sheet 18, the positive image is available for differential reception of a printing ink and may therefore be employed in conventional lithographic procedures for making ink copies.

FIGS. 2-4 illustrated a method for producing a photolithographic printing surface in accordance with the method disclosed in U.S. patent application Ser. No. 676,510 and that method will be better understood by reference to said drawings. FIG. 2 shows a silver transfer image formed on an image-receiving element comprising a silver-receptive stratum 40 contained on a suitable layer or member 46. The image is shown to have areas of silver 42 and non-image or highlight areas 44. As shown in FIG. 3, following treatment in accordance with the invention disclosed in U.S. patent application Ser. No. 676,510 with water or an aqueous medium at some time after image formation, removal of silver and areas of

stratum 40 corresponding thereto is selectively effected, the removed portions being indicated at 48.

The light-sensitive silver halide emulsion may be contained on a support or layer other than that bearing the silver-receptive stratum, i.e., the emulsion and the silver-receptive stratum may be present initially on separate elements or sheets, in which case the respective elements are brought into superposition during processing to provide the silver transfer image. Alternatively, they may be present initially as a unitary film unit. For example, the emulsion layer may be disposed over the silver-receptive stratum, in which case the emulsion and silver-receptive stratum are separated or peeled apart following processing to reveal the silver transfer image.

A unitary film unit of this description during processing thereof is illustrated in FIG. 4. As shown therein, such a film unit may contain a hydrophobic layer or support 56 having thereon an image-receiving layer 50, and a photosensitive silver halide emulsion layer 58. Development of an exposed film unit of this description is shown to be accomplished by spreading of a processing composition 52 over the surface of the photosensitive layer 58 with the aid of a spreader sheet or similar element 54.

Either of the aforementioned diffusion transfer systems provide excellent inking masters for producing ink copies of the original by conventional techniques, e.g., with conventional printing processes.

The following example illustrates the practice of the present invention.

EXAMPLES

A silver image-printing plate was prepared in the manner described in U.S. Pat. No. 3,220,837 by exposing a light-sensitive silver halide emulsion to form a developable image of the subject matter to be reproduced and thereafter applying an aqueous alkaline processing composition between the thus exposed emulsion and a superposed image-receiving element to develop the image and to impart to the image-receiving element a positive silver transfer image characterized as having image areas containing silver concentrated primarily at the surface in dense oleophilic masks and non-image (highlight) areas which are hydrophilic. An aqueous solution of ½% gelatin mixed in a 3:1 ratio with commercially available Ludox (30% silica L.S. type) was applied by brush to the positive image pattern in a fashion so as to eliminate selected oleophilic portions to provide a border about the print of FIG. 5.

The positive image pattern was then swabbed with a solution of the following formulation:

Water	cc	67.0
Glycerine	cc	30.0
Formaldehyde	g	1.0
Monobasic ammonium phosphate	g	2.0

The print then was rolled with a greasy ink sold by Multilith Corporation under the trade designation "Duro Clear Writing Fluid No. 40-2516A." This ink adhered only to the silvered portions of silver-receptive stratum 26 and did not adhere to the coated portion of the print. Finally, the print was pressed into contact with copy paper by means of a heavy steel roller to provide ink reproductions of the modified positive image pattern as shown in FIG. 6.

As can be seen from the above example, selected portions of the hydrophobic printing pattern may be effectively eliminated by applying a solution of the present invention such as a solution of ½% gelatin mixed in a 3:1 ratio with Ludox, to the selected portions. As stated, the solution or dispersions that can provide the hydrophilic coatings of the present invention can be applied to the selected hydrophobic portions by a brush, pen or by stamping in any preselected pattern. Accordingly, artistic designs such as borders of any desired pattern can be installed about the printing pattern. Also, information in

the form of written or printed instructions or signatures can be added to the printing plate by applying the hydrophilic coating in the desired pattern to preselected portions of the plate.

Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a process of forming a diffusion transfer lithographic printing master by developing an exposed light-sensitive silver halide emulsion containing a developable image with an aqueous alkaline processing composition, forming as a function of development an imagewise distribution of a soluble silver complex which is transferred, at least in part, by imbibition to a superposed image-receiving element comprising a hydrophilic silver-receptive stratum where said soluble silver complex is reduced to image silver to provide a hydrophobic printing pattern corresponding to said image silver, the step which comprises masking selected portions of said hydrophobic printing pattern by applying a hydrophilic coating to said selected portions, thereby rendering said selected portions hydrophilic and non-receptive to lithographic printing inks.

2. A process of claim 1 wherein said hydrophilic coating is applied to said selected hydrophobic portions as a solution or dispersion comprising a hydrophilic siliceous containing material.

3. A process of claim 2 wherein said solution or dispersion further includes a thickening agent.

4. A process of claim 1 wherein said siliceous containing material is a colloidal or finely divided oxide of silicon.

5. A process of claim 2 wherein said solution or dispersion comprises a colloidal or finely divided oxide of silicon and a polymeric thickening agent.

6. A process of claim 5 wherein said thickening agent is gelatin.

7. A process of claim 1 wherein said image silver providing the initial hydrophobic printing pattern is prepared by applying to a photoexposed gelatino silver halide stratum and a silver-receptive stratum, an aqueous alkaline solution of a silver halide developer and a silver halide solvent fixer, reducing exposed silver halide in the silver halide stratum to silver, forming from unreduced silver halide in the silver halide stratum a water-soluble complex silver salt, diffusing the salt to the silver-receptive stratum, producing from the salt on the silver-receptive stratum a visible image, said image having first areas that contain silver concentrated primarily at the surface of said silver-receptive stratum in thin but essentially continuous dense masses and second areas that are substantially silver free and stripping the silver halide stratum from the silver-receptive stratum.

8. A process of claim 1 wherein said image silver providing the initial hydrophobic printing pattern is pre-

pared by the steps of developing an exposed light-sensitive silver halide emulsion containing a developable image with an aqueous alkaline processing composition, forming as a function of development an imagewise distribution of a soluble silver complex which is transferred, at least in part, by imbibition, to a superposed image-receiving element comprising a hydrophilic silver-receptive stratum disposed on a hydrophobic layer or support member where said soluble silver complex is reduced to image silver to impart to said hydrophilic stratum a relatively dense silver transfer image; and wherein said silver transfer image is formed in the presence of an anti-adhesion reagent which penetrates the interstices of the silver-receptive stratum and selectively precludes adhesion of said stratum to said hydrophobic layer therebeneath in said areas of relatively dense silver deposit and thereafter contacting said silver-receptive stratum containing the silver transfer image with an aqueous medium for a time sufficient to remove said silver and said corresponding areas of said silver-receptive stratum.

9. A photolithographic printing plate having a hydrophobic printing pattern established on a hydrophilic silver-receptive stratum by the reduction of an imagewise distribution of a soluble silver complex transferred to said stratum and wherein selected portions of said hydrophobic printing pattern are coated with a hydrophilic coating to render said selected portions non-receptive to lithographic printing inks.

10. A photolithographic printing plate of claim 9 wherein said hydrophobic printing pattern comprises silver concentrated primarily at the surface of said silver-receptive stratum in thin but essentially continuous dense masses.

11. A photolithographic plate of claim 9 wherein said plate comprises a hydrophilic silver-receptive stratum disposed on a hydrophobic layer or support and wherein said hydrophobic printing pattern is established on said plate by transferring to said hydrophilic silver-receptive stratum an imagewise distribution of a soluble silver complex and forming a silver transfer image to provide a relatively dense silver transfer image therein in the presence of an anti-adhesion reagent which penetrates the interstices of said silver-receptive stratum and a selectively precludes adhesion of said stratum to said hydrophobic layer therebeneath in said areas of relatively dense silver deposit and said silver image is contacted with an aqueous medium for a time sufficient to remove said silver and said corresponding area of said silver-receptive stratum.

References Cited

UNITED STATES PATENTS

3,220,837 11/1965 Land et al. 96—29
2,732,796 1/1956 Van Dusen 101—465

NORMAN G. TORCHIN, Primary Examiner

J. L. GOODROW, Assistant Examiner

U.S. Cl. X.R.

96—33; 101—465

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,690,883 Dated September 12, 1972

Inventor(s) A. L. Hyland, Jr.

It is certified that error appears in the above-identified patent
and that said Letters Patent are hereby corrected as shown below:

Claim 4, line 1 (Column 5, line 33)
change "1" to --2--

Claim 7, line 9 (Column 5, line 49)
change "silvre" to --silver--

Claim 11, line 10 (Column 6, line 42)
delete "a" between --stratum-- and --selectively--

Signed and sealed this 22nd day of May 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents